

# PATENT SPECIFICATION

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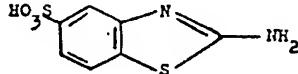


## (54) 2-AMINO-1,3-BENZTHIAZOLE-5-SULPHONIC ACID

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 According to the invention there is provided 2-amino-1,3-benzthiazole-5-sulphonic acid 5 which has the structure:

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and which may be prepared by the reduction of 3-nitro-4-thiocyanobenzene sulphonic acid. A method known *per se* may be used for the reduction. Thus, the nitro compound may be hydrogenated over a catalyst, for example a nickel or palladium on charcoal catalyst or an iron/acid reduction may be used. Other suitable methods, already known for the reduction of aromatic nitro compounds to aromatic amines, include electrolytic reduction. It is believed that the 3-amino-4-thiocyanobenzene sulphonic acid is first formed and then cyclises spontaneously to the amino-benzthiazole sulphonic acid.

20 The 3-nitro-4-thiocyanobenzene sulphonic acid may itself be prepared by a Sandmeyer reaction, that is to say by reacting diazotised 4-amino-3-nitrobenzene sulphonic acid with thiocyanate ions in the presence of cuprous ions.

25 A particularly convenient method of preparing the 2-amino-1,3-benzthiazole-5-sulphonic acid is to carry out the aforesaid Sandmeyer reaction on the 4-amino-3-nitrobenzene sulphonic acid and then reduce the reaction product without isolating the 3-nitro-4-thiocyanobenzene sulphonic acid. The overall yield using this method is approximately 90% of the theoretical yield.

30 If desired, the 2-amino-1,3-benzthiazole-5-sulphonic acid may be isolated in the form of one of its salts, for example an alkali metal or ammonium salt.

35 The new acid (or a salt thereof) may be used as a diazo component in the manufacture of azo dyes. Such dyes may be manufactured by coupling the diazotised 2-amino-1,3-benzthiazole-5-sulphonic acid with a coupling component of the pyrazolone, aminopyrazole, 2,6-dihydroxypyridine, 2,6-diaminopyridine, indole or arylamine series and may be used as acid dyes for the colouration of polyamide textile materials. It has the advantage over isomeric compounds, such as 2-amino-1,3-benzthiazole-6-sulphonic acid, that it can be prepared in good yield from readily available intermediates by relatively simple aqueous processes.

40 The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight.

### Example 1

45 24 parts of 4-amino-3-nitrobenzene sulphonic acid sodium salt are dissolved in 125 parts of 1 molar sulphuric acid with stirring and the solution is cooled to 0°C and diazotised by the slow addition of 50 parts of 2 molar sodium nitrite solution. 15 parts of sodium acetate are then added and the mixture is added to a stirred solution of 15.2 parts of ammonium thiocyanate and 0.5 parts of cuprous thiocyanate dissolved in 200 parts of water. After 2 hrs, the evolution of nitrogen has ceased and no diazonium salt can be detected in the mixture. 40 parts of sodium chloride are added and, after stirring a further 10 minutes, the crystalline precipitate is collected

by filtration, washed with a little 10% brine and dried. The yield of 3-nitro-4-thiocyanobenzene sulphonic acid sodium salt is 26.5 parts. An infra red spectrum of the product shows a characteristic thiocyanato absorption peak at 2170 cm<sup>-1</sup>.

5.64 parts of the 3-nitro-4-thiocyanobenzene sulphonic acid are dissolved in 100 parts of water 5  
 5 and the solution is hydrogenated at room temperature and 1 atmosphere pressure of hydrogen over 0.5 part of a 5% palladium on charcoal catalyst. When the theoretical volume of 1.34 litres of hydrogen has been absorbed, the solution is separated from the catalyst and acidified by the addition of hydrochloric acid. The white precipitate is collected by filtration washed with water and dried at 120°C in air. 4.6 parts of 2-amino-1,3-benzthiazole-5-sulphonic acid are obtained. 10  
 10 Elementary analysis of the product gives the following composition:-  
 Carbon - 36.5%, Hydrogen 2.4%, Nitrogen 12.1%  
 $C_7H_6N_2O_3S_2$  requires:- Carbon 36.52%, Hydrogen 2.60%, Nitrogen 12.17%  
*Example 2*  
 A mixture of 25 parts of iron filings, 100 parts of water and 0.5 parts of 36% hydrochloric acid 15  
 15 is stirred for 30 minutes at a temperature of 95°C. 14.1 parts of 3-nitro-4-thiocyanobenzene sulphonic acid are then added and vigorous stirring at 90-95°C continued for a further 2 hours. The mixture is then made alkaline by the addition of 2 parts of sodium carbonate and filtered. The clear filtrates are acidified by the addition of hydrochloric acid and the precipitate which 20  
 20 separates is collected by filtration, washed with water and dried at 120°C. 10.35 parts of 2-amino-1,3-benzthiazole-5-sulphonic acid are thus obtained.

*Example 3*  
 24 parts of 4-amino-3-nitrobenzene sulphonic acid sodium salt are dissolved in 125 parts of 1 molar sulphuric acid with stirring and the solution is cooled to 0°C and diazotised by the slow 25  
 25 addition of 50 parts of 2 molar sodium nitrite solution. 15 parts of sodium acetate are then added and the mixture is added to a stirred solution of 15.2 parts of ammonium thiocyanate and 0.5 part of cuprous thiocyanate dissolved in 200 parts of water. After 2 hours the evolution of nitrogen has ceased and no diazonium salt can be detected in the reaction mixture. The whole mixture is then added to a mixture of 50 parts of iron filings, 100 parts of water and 1 part of 36% hydrochloric acid, which has previously been stirred and heated at 95°C for a period of 30 30  
 30 minutes, and stirring at 90-95°C is continued for 2 hours. The mixture is then made alkaline by the addition of 4 parts of sodium carbonate and filtered. The clear filtrates are acidified by the addition of hydrochloric acid and the precipitate thus formed is collected by filtration, washed with water and dried at 120°C. 21 parts of 2-amino-1,3-benzthiazole-5-sulphonic acid are thus obtained.

35 **WHAT WE CLAIM IS**  
 1. 2-Amino-1,3-benzthiazole-5-sulphonic acid.  
 2. A process for the preparation of 2-amino-1,3-benzthiazole-5-sulphonic acid which 40  
 40 comprises reducing 3-nitro-4-thiocyanobenzene sulphonic acid by a known reduction method.  
 3. A process as claimed in claim 2 wherein the 3-nitro-4-thiocyanobenzene sulphonic acid is obtained by reacting diazotised 4-amino-3-nitrobenzene sulphonic acid with thiocyanate ions in the presence of cuprous ions and is reduced without being isolated.  
 4. A process as claimed in claim 2 conducted substantially as hereinbefore described with 45  
 45 reference to Example 1 or Example 2.  
 5. A process as claimed in claim 3 conducted substantially as hereinbefore described with reference to Example 3.  
 6. 2-Amino-1,3-benzthiazole-5-sulphonic acid whenever prepared by a process claimed in any one of claims 2 to 5.

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